A STUDY OF THE CORRELATION OF ELECTRICAL AND STRUCTURAL PROPERTIES OF PLATES IN THE LEAD STORAGE BATTERY

BY
STANLEY FELIX KERN
B.S., College of St. Thomas, 1937

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

URBANA, ILLINOIS
1941

A STUDY OF THE CORRELATION OF ELECTRICAL AND STRUCTURAL PROPERTIES OF PLATES IN THE LEAD STORAGE BATTERY

BY
STANLEY FELIX KERN
B.S., College of St. Thomas, 1937

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

URBANA, ILLINOIS
1941

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor George L. Clark, under whose direction and guidance this research was carried out, for his many suggestions and encouragement throughout the course of the work. He also feels greatly indebted to Dr. J. N. Mrgudich and Dr. S. T. Gross for many valuable suggestions and for the interest they have shown in the investigation.

Part I

A STUDY OF THE ANODIC POTENTIAL OF THE LEAD STORAGE BATTERY DURING FORMATION

Introduction

The potential of the positive plate of a storage battery during formation does not behave as would be expected from a simple application of the Nernst expression. The curve obtained when the anode potential is plotted against time of charge, rate of charge being held constant, shows a minimum value of the potential, sometime after the charging is begun. It was desired to investigate the factors affecting the nature of this minimum and to attempt an explanation for this behavior.

Experimental

Sections cut from green commercial plates were used as the plates. The potential during charge was measured against a cadmium - cadmium sulfate dummy[1] electrode by means of a potentiometer arrangement of the usual type.

The effect of three variables—temperature, concentration, and composition of the green plate—was studied.

Results

Curves obtained from plates after being pickled, soaked in sulfuric acid and thereby converting the PbO to $PbSO_4$, had no minimum. This fact indicated that the minimum was related to the reaction of PbO with H_2SO_4. An increase in temperature or of acid concentration decreases the time to obtain a minimum and therefore increases the rate at which sulfuric acid comes in contact with the PbO. The rapid rise of the potential after the minimum, when plates are charged in a high concentration of acid, indicates that the concentration of the acid in the pores of the plate determines to a great extent the potential at this stage of charging.

X-ray diffraction studies on positive plate surfaces show the presence of a carbonate and a highly perfected small particle size $PbSO_4$ which are not easily oxidized to PbO_2. It is also known that the molal volume of $PbSO_4$ is greater than the lead oxides resulting in a decrease in porosity on the surface of the plate. This situation would prevent the diffusion of sulfuric acid into the plate and since no conducting media is present, we would have a high internal resistance of the plate until this surface layer was destroyed.

Conclusion

The initial high potential of the positive plate is due to the large internal resistance of the plate itself. As charging proceeds the resistance decreases to a minimum value by virtue of complete penetration of the sulfuric acid into the pores of the plate and the destruction of the poorly "forming" surface compounds. The minimum point of the potential curve is indicative of a state of equilibrium between the diffusion of sulfuric acid into the plate, the formation of sulfuric acid in the charging process and the reaction of the sulfuric acid with PbO to form $PbSO_4$. After all of the available PbO present has been converted to the sulfate the concentration of the sulfuric acid within the pores of the plates increases with the subsequent increase in potential. The concentration of the acid will increase until the differential concentration between the acid within the pores and the main body of the electrolyte is such that the rate of diffusion out of the plate is equal to the rate of formation of sulfuric acid by the charging process. At this point the potential becomes reasonably constant and maintains this value until near the end of the formation when another increase is observed, due to the evolution of oxygen.

Part II

THE EFFECT OF GRINDING ON THE X-RAY DIFFRACTION PATTERNS OF SYSTEMS CONTAINING LEAD OXIDES

Introduction

The X-ray diffraction method is recognized as a valuable tool in following the reactions taking place in the manufacture and use of the lead storage battery. The actual limits of detection of one compound in the presence of another by X-ray diffraction methods is not very well known. The object of this investigation was to attempt to set up these approximate limits. In the preparation of these samples in a form suitable for giving the best type of X-ray diffraction patterns, it was found necessary to grind some of the materials used. It has been known for sometime that grinding alters the X-ray diffraction patterns of some of these materials. Hence, it was decided to study at the same time the effect of grinding on these mixtures.

Experimental

Six binary systems involving the lead oxides were investigated using six to eight different percentage compositions of each. These mixtures were ground in an agate mortar reserving samples at various times of grinding for X-ray diffraction studies. In this manner twenty to thirty patterns were obtained to describe each of the following systems: Y PbO-PbO_2, R PbO-PbO_2, R PbO-$PbSO_4$, $PbSO_4$-PbO_2, R PbO-PbI_2, and Y PbO-PbI_2.

The grinding was carried out manually and in contact with the atmosphere in all cases except for a few samples of PbO-PbO_2. Some of these were ground in an atmosphere rich in nitrogen and the rest in a partial vacuum.

Results

1. Grinding mixtures of PbO_2 with either R PbO or

Y PbO results in the disappearance of the X-ray diffraction lines characteristic of PbO.

A. Active oxygen analysis on the samples before and after grinding showed that there was no increase in oxygen content in the mixture during grinding and consequently no oxidation of PbO to PbO_2.

B. The formation of a solid solution of PbO in PbO_2 or compound formation between them is improbable as the PbO is easily extracted from the ground mixture with sulfamic acid, no new lines indicative of compound formation are present on the pattern, and on annealing the ground sample the PbO is restored to normal PbO.

C. There is an abnormally high absorption of CO_2 by the PbO when ground. The absorption of CO_2 is not the cause of the disappearance of the PbO pattern as the PbO lines do not appear on patterns ground in vacuum and containing less than 0.1 percent CO_2.

D. The high absorption of CO_2 by the mixture when ground in air is further evidence of the increased activity of PbO when formed in the distorted state.

2. Lead Oxide loses its diffracting power when ground with other compounds such as $PbSO_4$.

3. Grinding mixtures of PbI_2 and PbO results in the disappearance of the pattern of the PbI_2 while the PbO pattern remains.

Conclusion

Lead Iodide when used as the impurity and ground with PbO acts as a lubricant and thereby protects the PbO from distortion. This lubricating action of the PbI_2 arises from the weak forces existing between layers of iodine ions in the PbI_2 crystals.

The destruction of the diffracting ability of the PbO when

ground with PbO_2 is probably a result of the abrasive action of the extremely hard PbO_2 crystals.

Bibliography

1. Vinal, G. W., "Storage Batteries," 2nd Ed., John Wiley and Sons, (1930), P. 221.

VITA

The author was born November 20, 1913, in Bechyn, Minnesota. He received his elementary training in the Parochial Grade School and his secondary education in the Public High School of Olivia, Minnesota. He entered St. Thomas College in St. Paul, Minnesota in the fall of 1933, and was graduated with the degree of Bachelor of Science in Chemistry in 1937.

During the school year 1937-38 he attended the Georgia School of Technology while working for the Georgia State Experiment Station. He entered the Graduate School of the University of Illinois in the fall of 1938 and has been an assistant in the Analytical Division during the years 1938-39, 1939-40, 1940-41.

He is a member of Sigma Xi, Phi Lambda Upsilon, and the American Chemical Society.